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HYDROGEN BONDING IN NITROCELLULOSE
AND ITS IMPLICATIONS ON
DETERRING OF SMALL ARMS PROPELLANT

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Hydrogen Bonding in Nitrocellulose and Its Implications on Deterring of Small Arms Propellant

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ABSTRACT

The hydrogen bonding characteristics of well-characterized nitrocellulose samples were studied by means of IR spectroscopy. Results obtained for nitrocellulose samples of varying nitrogen content showed that the strength of the hydrogen bond increases with decreasing nitrogen content. In addition, atmospheric moisture was found to hydrogen bond with nitrocellulose hydroxyl groups. The implications of these findings on the deterring phase of the small arms propellant manufacturing process are discussed.

INTRODUCTION

A previous study [1] established that hydrogen bonding occurs between small arms propellant burning rate modifiers which are called deterrents (di-n-butyl phthalate, camphor, ethyl centralite, and methyl

centralite) and unesterified hydroxyl groups in nitrocellulose (NC). These deterrent molecules are diffused into the spherical NC-based small arms propellant grains in order to reduce the initial burning rate of the propellant bed when the surface area is at maximum. A knowledge of the concentration profile of the deterrent molecule as a function of distance into the grain as well as the physical and chemical interactions involved is important for interior ballistic computer simulation and a host of manufacturing and storage problems. An important consideration in describing the deterring mechanism is a determination of the factors which would reduce the possibility of hydrogen bonding between deterrent molecules and NC hydroxyl groups. For this reason a detailed study of hydroxyl interaction in well-characterized NC samples was performed.

A previous study based on measurement of γ -OH in the IR region indicated that hydrogen bonding may occur in NC films. Cherubin [2] determined the γ -OH for NC films having two different nitration levels (11.8 and 5.7%N) and cellulose. The reported γ -OH for NC of 11.8%N was 3559 cm^{-1} , for 5.7%N was 3597 cm^{-1} , and for cellulose was 3356 cm^{-1} . These NC samples were not well characterized and no molecular weight or viscosity data was given. Based on this data, it appears that the author concluded that hydrogen bonding does occur in NC and that it is enhanced by increasing nitrate ester presence.

It should be pointed out that the 11.8%N NC corresponds to 0.8 hydroxyl groups per repeat unit and that the 5.7%N NC corresponds to 2.20 hydroxyl groups per repeat unit. This raises the possibility that hydrogen bonding occurred within a repeat unit in the 5.7%N NC.

EXPERIMENTAL

The five well-characterized NC samples used in this study were obtained from Picatinny Arsenal. Raw NC samples obtained from Hercules, Inc. were dissolved in acetone and then fractional precipitation was accomplished by means of the addition of various water/acetone solutions having increasing water content. Data for number and weight-average molecular weight calculations were obtained from a Waters Model 200 gel permeation chromatograph. The solvent used in all cases for the gel permeation chromatography was acetone and the support medium was Porasil. Five 4-ft columns of varying permeability Porasil 1500X, 1000X, 400X, 250X, and 60X were used.

Nine polystyrene standards obtained from Waters were used to calibrate the chromatograph. These standards ranged in molecular weight from 5,000 to 2,610,000. Number- and weight-average molecular weights for the nitrocellulose were calculated using the summation of heights method and are given in Table 1. NC samples of narrow molecular weight distribution are not commercially available and this is the reason for the use of polystyrene standards. It

TABLE 1. Molecular Weight Data for Various Nitrogen Content NC Samples

%N in NC	M_w	M_n	M_w/M_n
12.10	141,500	84,500	1.67
12.20	154,800	92,400	1.68
12.30	230,400	224,800	1.03
12.60	139,600	90,450	1.54
13.16	128,200	76,000	1.69

should be pointed out that since the M_w and M_n were calculated from the chromatographic data, they are strongly dependent on the standards used to calibrate the GPC system. For this reason the data are not as accurate as one would want. However, the data does show the relative trends between samples with sufficient accuracy.

All of the NC samples were dissolved in MC&B reagent grade ethyl acetate, and these solutions were cast as films on salt plates. After film casting, the plates were placed in a vacuum desiccator and subjected to a roughing pump vacuum for several hours. IR spectra for each sample were run with and without a dry air purge. All spectra were obtained on a Perkin-Elmer IR spectrophotometer model 621.

DISCUSSION

The γ -OH for the NC samples described in the experimental section were measured in the IR region and are reported in Table 2. Significant interactions within a repeat unit were excluded since the range of the nitrogen content of the samples used corresponds to less than one hydroxyl group per repeat unit. Table 2 includes the γ -OH for each sample measured in atmosphere and under a dry air purge. It can be seen that in all cases the γ -OH for the samples measured in air were shifted to lower frequencies. Further, a broad peak from 3620 - 3680 cm^{-1} (with numerous shoulders) was present in all samples run in air but was absent in all samples run under the dry air purge.

Measurement of γ -OH in air did not give reproducible results as evidenced by the wide range of values reported in Table 2. This was not the case for the samples run under purge conditions.

Therefore, it appears that atmospheric moisture is involved in a NC hydroxyl group interaction. In order to gain further insight into the suspected water-NC interaction, several spectra were run of NC

TABLE 2. γ -OH for Various Nitrogen Content NC Samples

% N in NC	γ -OH ^a (cm ⁻¹)	γ -OH ^b (cm ⁻¹)
12.10	3514	3525
12.20	3502-3536	3544
12.30	3514	3538-3540
12.60	3528-3532	3558
13.16	3528-3550	3560

^aRun in air, expanded spectra (represents five runs).

^bRun under purge condition, expanded spectra (represents five runs).

exposed to deuterium oxide. The only noticeable effect was a significant reduction in intensity of the 3620-3680 cm⁻¹ peak. Unfortunately, the D₂O related shift of the 3620-3680 cm⁻¹ peak could not be observed, either because of low intensity or interference with a NC and D₂O peak. Another complicating factor was the presence of some H₂O-NC interaction as evidenced by the persistence of a peak at 3620-3680 cm⁻¹.

Examination of the data for the purge runs shows a trend toward higher frequencies with increasing nitrogen content. The only exception is the 12.3%N NC sample. This trend corresponds to stronger hydrogen bond formation with increasing number of hydroxyl groups. The four samples which followed this trend had a very similar M_w/M_n (Table 1), while the 12.3%N NC had a significantly lower value, indicating a much narrower molecular weight distribution. It therefore appears that the molecular weight uniformity of NC influences the strength of the hydrogen bonds.

The findings of this study are contrary to the conclusion of Cherubin [2] who believes that the -ONO₂ group participated in hydrogen bonding and that an increase in nitrogen content led to strong hydrogen bonds. The spectra for each sample used in this study were examined in the -ONO₂ asymmetric stretch region (1650 cm⁻¹) [3] and no shift was observed. Thus it appears that the -ONO₂ group does not participate in hydrogen bonding under these conditions. The conclusions of this study are that hydrogen bonding does occur in NC and that this bonding is only due to hydroxyl interactions. Further, the strength of this interaction increases with the number of OH groups present. Finally, the NC-OH groups can enter into weak hydrogen bonding with water.

The implications of these findings on the deterrent concentration profile for small arms propellant will now be briefly discussed.

Interaction between NC hydroxyl groups are in all cases weaker than the deterrent carbonyl-NC hydroxyl interaction. With higher nitrogen contents, the NC-OH interaction becomes even weaker. The weakest interaction obtained in this study was with the 13.1%N NC which is approximately the nitrogen content used for small arms propellants. Therefore, it appears that the interaction between NC hydroxyl groups would not prevent the bonding of deterrent during impregnation.

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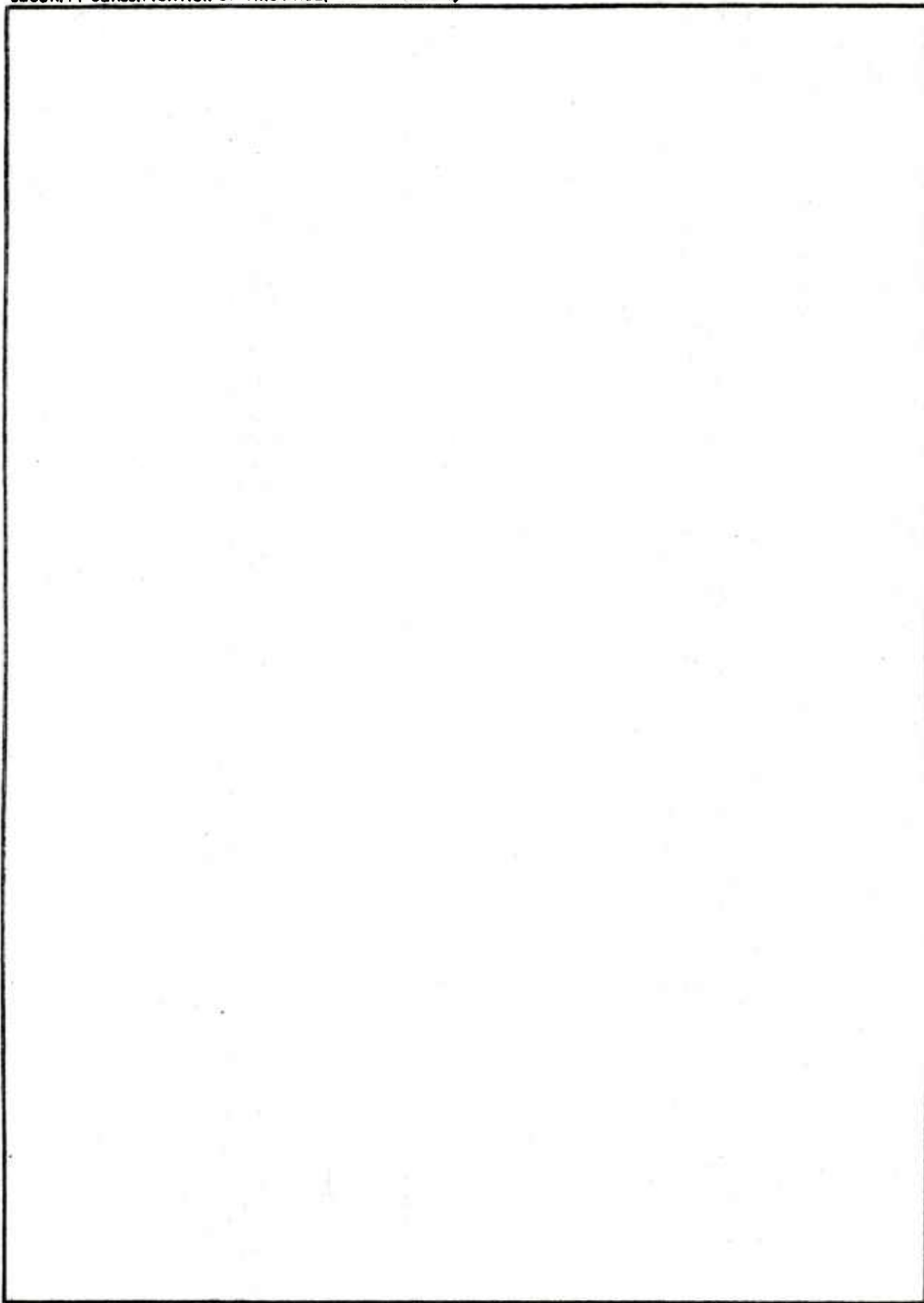
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